



Development of analytical methods for polycyclic aromatic hydrocarbons (PAHs) in airborne particulates: A review

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Abstract

In the present work, the different sample collection, pretreatment and analytical methods for polycyclic aromatic hydrocarbons (PAHs) in airborne particulates is systematically reviewed, and the applications of these pretreatment and analytical methods for PAHs are compared in detail. Some comments on the future expectation are also presented.

Key words: polycyclic aromatic hydrocarbons (PAHs); airborne particulates; analytical methods; review

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of several hundred individual compounds defined to be composed of two or more fused aromatic rings. PAHs are of concern because certain of them are classified as probable human carcinogens (IARC, 1983; IPCS, 1998; UNECE, 1998; Vestreng and Klein, 2002) and show tumorigenic activity and endocrine disrupting activity in mammals (Cavalieri and Rogan, 1998). Recently the regulations of PAHs have been enacted or proposed in Europe and by the WHO (Bostrom *et al.*, 2002; WHO, 2000; WHO/IPCS, 1998).

Unsubstituted PAHs are formed mainly by the incomplete combustion of organic materials (Baek *et al.*, 1991; Mastral *et al.*, 2000a). And the atmospheric photochemical PAH reactions cause to form many kinds of substituted PAHs, such as nitrated PAHs (NPAHs), hydroxylated PAHs (OH-PAHs), amino-PAHs (APAHs) and so on. For example, NPAHs are formed easily by the reaction of PAH with reactive species found in ambient air, such as dinitrogen pentoxide (N₂O₅) and oxygen radicals in the presence of nitrogen oxides and hydroxylated radicals. During the last three decades, a great deal of health research interest focused on the mutagenicity and carcinogenicity of PAHs and their oxidation products (Ames *et al.*, 1975; Finlayson-Pitts and Pitts, 1999; Mersch-Sundermann *et al.*, 1993). And

the results showed some of substituted PAHs may be more toxic than the parent PAHs. PAHs and their derivatives are directly emitted by diesel and petrol engines, industrial processes, coal combustion, cigarette smoke, and have also been found in carbon black and photocopier toners, fly ash, exhaust emission from waste incineration plants (Barzegar and Dasgupta, 1996; Cvacka *et al.*, 1998; Jacob *et al.*, 1991; Kirton and Crisp, 1990; Lee *et al.*, 1998; Marr *et al.*, 1999; Mastral *et al.*, 1999; Moreira *et al.*, 1996; Oamh *et al.*, 1999; Wilhelm *et al.*, 2000; Xu *et al.*, 2006; Zimmermann *et al.*, 1999). Hayakawa *et al.* (1995a, 1995b) reported that automobiles are a main source of atmospheric PAHs and NPAHs. PAHs and their derivatives need to be monitored in time, which is benefit to value the quality of air and infer the source of pollutants.

Due to the PAHs high volatility, PAHs from energy generation can be released both supported onto the particulate matter (PM) and/or in the gas phase (Mastral *et al.*, 2000b, 2001). The most volatile compounds with two or three aromatic rings, are mainly released in the gas phase, while compounds containing more than three aromatic rings, are generally associated with the PM emission. The PAHs gas/solid partitioning is related to many different variables like the liquid vapor pressure, the ambient temperature and the size, chemical composition and surface area of the PM. These characteristics, together with the PAHs volatile character, will determine the way in which they are emitted to the atmosphere. The U.S. Environmental Protection Agency (EPA) promulgated a new size-specific air quality standard for environmental particulate matter in 1987 (EPA, 1987). This new standard

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applies only to particulate with diameters smaller than or equal to 10 μm (PM_{10}) and replaces the original standard for total suspended particulate matter (TSP). Nowadays, $\text{PM}_{2.5}$ and aerosols with 1.0 μm or less in diameter are being taken into account because they represent the particle fraction inhaled into the deeper respiratory tract regions. In addition, PAHs are concentrated in the submicro-PM due to gaseous PAHs condensation into the smallest particles.

Sensitive, rapid, simple and accurate methods have been developed to determine PAHs and their derivatives in the atmospheric particles. As high efficient separation tools, GC and HPLC have been used for determining all kinds of samples containing complex components. GC-FID, GC-MS, HPLC-FL (Silvestre *et al.*, 1986; Wilhelm *et al.*, 2000) are the conventional analytical methods to determine the unsubstituted PAHs. And the substituted PAHs, such as NPAHs, most of these compounds are low volatile and instable, are mainly determined by HPLC. And the continuing use of LC methods for the determination of NPAHs is documented by the increase in the number of published paper (Cvacka *et al.*, 1998). Method of the combination of HPLC with fluorescence (Tejada *et al.*, 1986), chemiluminescence (Hayakawa *et al.*, 1995a) and electrochemical detection (Jin and Rappaport, 1983; Kuo *et al.*, 2003) have been developed. GC-NPD and GC-NICIMS (David *et al.*, 1982) are also used for determining the 2- or 3-rings NPAHs and have good selectivity and sensitivity.

The direct determination of extremely trace PAHs and their derivatives by modern high efficient chromatographic techniques is still very difficult. The limitations are associated not only with the insufficient sensitivity of these techniques but with matrix interference. For this reason, the separation and preconcentration techniques are often required. For the atmospheric particulates sample, extraction methods of PAHs and their derivatives include traditional Soxhlet extraction, ultrasonic extraction, supercritical fluid extraction, microwave-assisted extraction and accelerated solvent extraction. Solid phase extraction is often followed for clean-up the interference of the extraction liquid.

But the analysis of atmospheric PAHs faces many problems: the airborne particulate samples are extremely complex, and often contain many different classes of compounds in varying amounts; many studies are incompatible due to differences in results caused by differences in analysis techniques: very low concentration required more sensitive analytical methods which are not suitable for larger quantities; the most common atmospheric PAHs sampling uses filters or adsorbents, which are not proper for the most volatile species and can be lost before detection and/or other species cannot be totally extracted once adsorbed; PAHs deposition with the PM greater than 3–5 μm and/or gas PAHs re-volatilisation once deposited; strong influence of the meteorological conditions; strong influence of the ambient contaminants, and so on.

Researchers in many countries have made much effort to the analysis of PAHs in airborne particulates. This paper summarizes the PAHs data in airborne particulates

to help understand the sample collection, pretreatment and analytical methods of PAHs.

1 Analytical methods for PAHs in airborne particulates

1.1 EPA standard analytical method for atmospheric PAHs

Under the sponsorship of EPA, Method TO-13 was originally published in March of 1989 as one of a series of peer-reviewed methods in the second supplement to “compendium of methods for the determination of toxic organic compounds in ambient air”, EPA 600/4-89-018. In an effort to keep these methods consistent with current technology, Method TO-13 has been revised and updated as Method TO-13A “determination of polycyclic aromatic hydrocarbons (PAHs) in ambient air using gas chromatography/mass spectrometry (GC/MS)”. This compendium incorporates new or improved sampling and analytical technologies. The summary of Method TO-13A is as following (EPA, 1999):

(1) Filters and sorbent cartridges (containing PUF or XAD-2) are cleaned in solvents and vacuum dried. The filters and sorbent cartridges are stored in screw-capped jars wrapped in aluminum foil (or otherwise protected from light) before careful installation on the sampler.

(2) Approximately 300 m^3 of air is drawn through the filter and sorbent cartridge using a high-volume flow rate air sampler or equivalent.

(3) The amount of air sampled through the filter and sorbent cartridge is recorded, and the filter and cartridge are placed in an appropriately labeled container and shipped along with blank filter and sorbent cartridges to the analytical laboratory for analysis.

(4) The filters and sorbent cartridge are extracted by Soxhlet extraction with appropriate solvent. The extract is concentrated by Kuderna-Danish (K-D) evaporator, followed by silica gel cleanup using column chromatography to remove potential interferences prior to analysis by GC/MS.

(5) The eluent is further concentrated by K-D evaporation, then analyzed by GC/MS. The analytical system is verified to be operating properly and calibrated with five concentration calibration solutions.

(6) A preliminary analysis of the sample extract is performed to check the system performance and to ensure that the samples are within the calibration range of the instrument. If the preliminary analysis indicates nonperformance, then recalibrate the instrument, adjust the amount of the sample injected, adjust the calibration solution concentration, and adjust the data processing system to reflect observed retention times, and so on.

(7) The samples and the blanks are analyzed and used (along with the amount of air sampled) to calculate the concentration of PAHs in the air sample.

1.2 Some analytical methods for atmospheric PAHs

With the development of technology, the analytical methods for PAHs are growing. It is probably true to

say that advances in environmental analyses have more or less occurred concomitantly with those in the analytical methods. A cursory examination of accepted and certified methods of analysis of many environmental pollutants indicates that chromatographic techniques play a significant role, and may well be the most widely used procedures in this area of application. More specifically, chromatography is a principal technique in the analysis of air pollutants; the continued advent of new or improved instrumentation and novel column technologies have meant that chromatography has remained at the forefront in this area of research, and its preeminent position appears unchallenged in the foreseeable future. A wide number of techniques have been developed for the determination of PAHs in the airborne particulate matter, such as thin-layer chromatography (TLC), gel-permeation chromatography (GPC), gas chromatography (GC), gas chromatography-mass spectrometry (GC/MS) and high-performance liquid chromatography (HPLC), etc. Chromatographic techniques such as GC or HPLC coupled with fluorescence, UV, FID and MS detectors are the most frequently used now. As reported, HPLC has been successfully used to analyze PAHs for more than twenty years. It has become one of the most effective methods for monitoring PAHs. Compared with GC method, HPLC, especially reverse phase HPLC (RP-HPLC), can analyze the compounds without the considering of volatility and molecular weight, moreover, it shows good selectivity and high sensitivity. HPLC with ultraviolet absorption detector or fluorescence detector was used to determine atmospheric PAHs by many groups (Lee and Lee, 2004; Li and Ro, 2000; Venkataraman *et al.*, 1999; Yutaka *et al.*, 2005; Zhu and Wang, 2003). GPC was found to be good for PAHs isomers and derivations (Fernandez and Baynoa, 1992; Lohmann *et al.*, 2001). GC/MS was also widely used in the determination of PAHs according to its superiority in qualitative and quantitative analysis (Allen *et al.*, 1996; Chen *et al.*, 2005; Gigliotti *et al.*, 2005; Lee *et al.*, 1995, 2001; Ochsenkuhn-Petropoulou *et al.*, 2003; Possanzini *et al.*, 2004).

In addition, some biologic methods also have been applied in the determination of PAHs. Li *et al.* (1999) developed sensitive enzyme-linked immunosorbent assays (ELISAs) for multianalyte detection of PAHs. The haptens with different lengths of carboxylic acid spacers at various positions were derived from PAHs. And these haptens were coupled with bovine serum albumin to form competitor conjugates. All of the haptens were recognized to different extents by monoclonal antibodies 4D5 and 10C10. Cigamek *et al.* (2004) realized a combined chemical and bioassay analysis of traffic-emitted PAHs. And Angerer *et al.* (1997) reviewed biological monitoring and biochemical effect monitoring of exposure to PAHs.

1.3 Analytical methods for nitro-PAHs and other PAHs derivatives

Oxygenated and nitro-substituted polycyclic aromatic hydrocarbons (oxy- and nitro-PAHs, respectively) are formed in the combustion of fuel, natural gas, wood,

coke and in residue incineration. They are present in tobacco smoke and also in the ambient air due to chemical reactions of PAHs with different atmospheric pollutants, such as NO_x or O_x (Alebic-Juretic *et al.*, 1990; Fan *et al.*, 1995; Pitts *et al.*, 1978; Xu and Burlingame, 1988). The direct mutagenic activity of tobacco smoke or atmospheric extracts has been mainly correlated with the presence of oxy- and nitro-PAHs (Bayona *et al.*, 1994; Casellas *et al.*, 1995; Yu *et al.*, 2002). While PAHs have proved to be indirect mutagens, nitro-PAHs are direct-acting mutagens.

Analytical techniques which have high resolution and specificity are required for the determination of a large number of NPAHs and related compounds in environmental samples. GC is used for determining nitro compounds because of its high resolution, sensitive and selective detection. Many types of detectors have been developed for nitro compounds. These include electron capture detector (ECD), nitrogen and phosphorus selective detector (NPD), thermionic ionization detector (TID) operated in a nitrogen atmosphere, chemiluminescence detector (CLD) and mass spectrometry (MS) (Marino *et al.*, 2000; Schnelle-Kreis *et al.*, 2001). The most selective and sensitive techniques for the detection of oxy- and nitro-PAHs are based on electron capture processes occurring in the gas phase, due to the electronegative character of the nitro and oxy groups conjugated with the aromatic rings. This allows the detection of low concentrations and a higher degree of selectivity than in other types of common detectors. Thus, negative ion chemical ionization mass spectrometry (NCI-MS) (Bezabeh *et al.*, 2003; Dusek *et al.*, 2002; Ramdahl and Urdal, 1982; Siegmund *et al.*, 2003) and ECD (Xu and Lee, 2001) are the most widely used techniques for the analysis of oxy- and nitro-PAHs, showing the lowest limits of detection. Xu and Lee (2000) also developed a derivatization-GC/ECD analytical method to identify and quantify NPAHs in atmospheric particulate matter.

The nitro-group of NPAHs is electrochemically, chemically or metal-catalytically reduced to a nitroso group, a hydroxyamino group and then an amino group (Hayakawa, 2000). The resulting amino-PAHs (APAHS) are fluorescent and this reaction pathway is very useful for the sensitive and selective detection of NPAHs. HPLC with different kinds of detection techniques for NPAHs has been reviewed (Cvacka *et al.*, 1998). NPAHs can be separately determined by HPLC with electrochemical detection (HPLC/ECD) (Galceran and Moyano, 1993). Other papers concerning HPLC with chemiluminescence and fluorescence detections (CLD and FLD) for NPAHs have also been reported or reviewed (Hayakawa *et al.*, 1992, 1999a, b; Taga *et al.*, 2005; Tang *et al.*, 2004). The schematic diagram of typical HPLC/CLD analytical system is shown in Fig.1 (Tang *et al.*, 2003). The HPLC system in Fig.1 was operated as follows. After the sample was introduced into the system, the NPAHs were separated from interfering substances on the clean-up column. Then by changing the position of the switching valve, the APAHS which were produced by passing the NPAHs through the reducer column, were concentrated on the concentrator column by adding the ascorbic acid solution from pump 2 to the

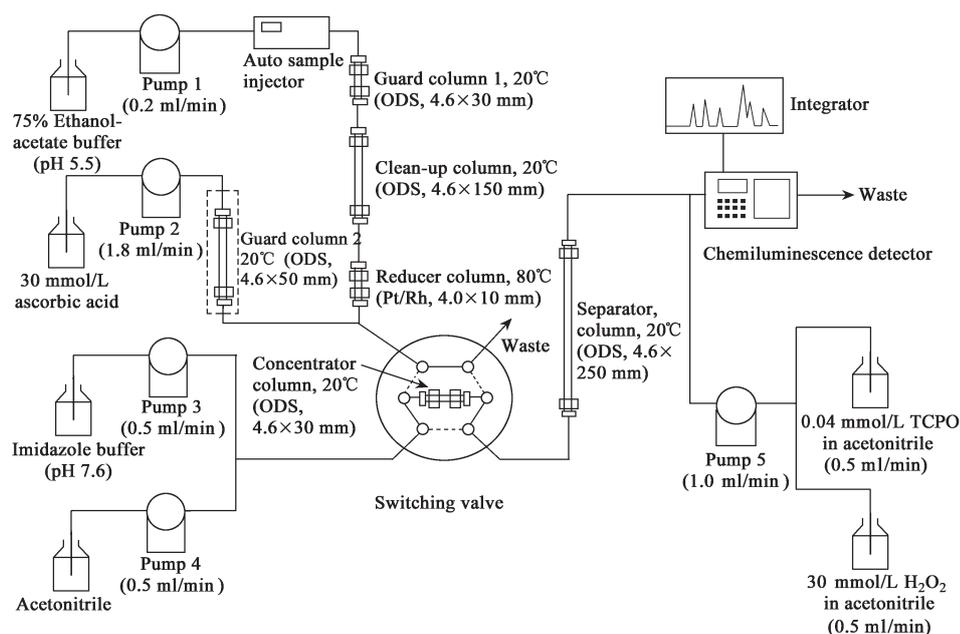


Fig. 1 Schematic diagram of typical HPLC/CLD analytical system (Tang *et al.*, 2003).

effluent from the reducer column to increase the water concentration. After all APAHs were eluted from the clean-up column and concentrated on the concentrator column completely, the APAHs were eluted into the separator column with a mixture of buffer (from pump 3) and acetonitrile (from pump 4) by changing the position of the switching valve. Then the APAHs are separated on the separator column and detected by chemiluminescence. And as mentioned above, NPAHs are not fluorescent but most APAHs are strongly fluorescent. So in order to apply HPLC/FLD to NPAHs, NPAHs must be reduced. Both off-line and on-line reduction methods have been reported (Hayakawa *et al.*, 1993, 2002; Murayama and Dasgupta, 1996). In addition, only a few studies have been reported concerning LC-MS of NPAHs (Bonfanti *et al.*, 1996). But the sensitivity of LC-MS is not enough for NPAHs at trace levels in environmental samples. A few studies concerned the analysis of PAHs and NPAHs by low-temperature Shpol'skii fluorescence/luminescence spectroscopy (Kozin *et al.*, 1996; Matsuzawa *et al.*, 1995).

2 Sampling and pretreatment methods for PAHs in airborne particulates

2.1 Sampling methods for PAHs

The sampling techniques for PAHs have been improved in last two decades. A number of researches showed that the main sampling modes for atmospheric PAHs are active sampling and passive sampling. The samplers used mainly are high-volume sampler and impingement cascade sampler. Sorbent, filter, impingement collector, etc. are usually used to collect target compounds in active sampling. And passive sampling is due to the migration of target compounds through concentration gradient. Passive sampling has been successfully applied to environmental

monitoring, particularly in the analysis of gaseous PAHs and other little organic compounds in the air. It is a popular sampling technique because it is portable, noiseless and lower cost. Semipermeable membrane devices (SPMDs) used as passive samplers have been reported (Soderstrom and Bergqvist, 2004; Soderstrom *et al.*, 2005). A standard semi-volatile sampling train with a filter was also used to collect PAHs (Sheu *et al.*, 1997).

In many applications, filters were used to collect the particle-bound PAHs while solid sorbent was used to collect gaseous volatile PAHs. As reported, glass fiber filter (Bi *et al.*, 2003; Lin *et al.*, 2002; Simcik *et al.*, 1999; Tsai *et al.*, 2002), quartz fiber filter (Gigliotti *et al.*, 2005; Okuda *et al.*, 2002), cellulose filter (Ochsenkuhn-Petropoulou *et al.*, 2003) were the filters mostly used to collect particle-bound PAHs. And the choice of sorbent is very important in the collection of gaseous volatile PAHs. The sorbent should have high collection efficiency, large adsorb capacity and chemical stability. Most sorbent used to collect gaseous PAHs were Tenax, XAD-2, polyurethane form (PUF), Florisil, Seppark-C₁₈ and so on. Thereinto PUF and XAD-2 are mostly used due to their advantages of low-cost and tractable.

For different size particles, there are some different methods to collect them. PM₁₀ and PM_{2.5} samples can both be collected by high-volume samplers. But for data comparison, low-volume sampler with 10 or 2.5 μm inlet was used to collect PM₁₀ and PM_{2.5} samples, respectively (Guo *et al.*, 2003). In addition, airborne particles were collected and size-fractionated using a sampler that combined a minipump with a three-stage cascade impactor. Different kinds of filters were used to collect different size particles (Ohura *et al.*, 2004).

It should be noted that it is better to reduce the sampling time especially in the collection of gaseous PAHs. Until now, both high-volume and low-volume samplers

can collect the particle-bound PAHs, but they have still needed some improvements to monitor the gaseous PAHs exactly. How to avoid the volatilization and loss of PAHs in the sampling, the reaction between PAHs and other compounds and the redistribution among different size particles still need more effort. A modified high-volume sampling—with an oxidant denuder system added, in order to minimize the PAH degradation during air sampling, was reported recently (Tsapakis and Stephanou, 2005a, b).

2.2 Preservation and pretreatment of air samples

2.2.1 Preservation of samples

Volatilization and loss of PAHs may occur on the filter and sorbent. So the preservation of samples should be very careful. Usually, each filter should be folded with the adsorbed particulate matter on the inner side, wrapped in an aluminum foil to protect them from light and kept under refrigeration at low temperature (about -18°C) until extraction and analysis (Dallarosa *et al.*, 2005a; Sanderson and Farant, 2005; Wu *et al.*, 2006).

2.2.2 Pretreatment of samples

The air matrix is complicated and the concentration of PAHs in the air is very low, so the pretreatment of samples is a very important step for the determination of PAHs. Song and Lin (2005) reviewed sample pretreatment techniques for PAHs in environmental matrix. Dichloromethane, acetonitrile, benzene, toluene, cyclohexane and their mixture are usually used as extraction solvent. Solvent extraction (such as Soxhlet extraction, ultrasonic extraction, supercritical fluid extraction (SFE), microwave-assisted extraction (Lee *et al.*, 2001), accelerated/pressurized solvent extraction), concentration (such as K-D evaporator (Bae *et al.*, 2002; Cecinato *et al.*, 1999; Zhang *et al.*, 2005) and rotary evaporator concentration (Chetwittayachan *et al.*, 2002)) and clean-up with columns (Hafner and Hites, 2005) are three mostly applied pretreatment methods for PAHs samples. And subcritical water extraction has also been applied as pretreatment of air samples (Romero *et al.*, 2002).

Soxhlet extraction is a classical method due to its high extraction efficiency. Yang *et al.* (1999) determined polycyclic aromatic hydrocarbon concentrations in extract solvent of airborne particulate in different steps of Soxhlet extraction, and drawn out the Soxhlet extraction curves, then found the extract efficient mainly depended on extract cycle numbers, did not depend on extract soak time. By comparing Soxhlet extract efficient of eleven kinds of extract solvents to adding standard reference matter and research reference matter, they found cyclohexane and benzene as extract solvents most in use were not so well efficient extract solvents. The order of extract efficient of the extract solvents is as follow: quinoline-ethanol, pyridine-ethanol, acetone, ethanol, dichloromethane, benzene, cyclohexane, petroleum ether, acetone-ethanol-cyclohexane, trichloromethane, and tetrahydrofuran. Dallarosa *et al.* (2005b) used Soxhlet extraction technique to identify and quantify the main sources of PAHs associated with aerosols (PM_{10}) collected at three different sampling sta-

tions. Fang *et al.* (2004) used dichloromethane/hexane as solvent to Soxhlet extract PAHs and simultaneously measured PAHs from 2002–2003. But it is time-consuming (about several hours) for the extraction of PAHs and further concentration need to do because of the large amount of solvent.

Ultrasonic extraction is a popular method for PAHs because it is time-saved, solvent-saved and high efficiency. Park *et al.* (2002) applied ultrasonic extraction for PAHs and followed by GC/MS determination. They analyzed the concentrations of PAHs in different sites in Korea. Some authors such as Hayakawa *et al.* (2002), Tang *et al.* (2005), Bi *et al.* (2005), Duan *et al.* (2005) all applied ultrasonic extraction technique.

Supercritical fluid extraction (SFE) also has been applied in the analysis of atmospheric PAHs. It has high extraction efficiency, good selectivity. It is time-saved and can not induce secondary pollution. What's more, it can be easily coupled with GC, GC-MS, HPLC, etc. Shimmo *et al.* (2004) analyzed the PAHs by on-line SFE-LC-GC-MS. The operation was simple and largely reduced the loss of targets. The solvent used in SFE usually are CO_2 , NH_3 , ethylene, ethane, N_2O , propane, propylene and H_2O . Castells *et al.* (2003) reported on the applicability of SFE for the analysis of oxy- and nitro-PAHs in particulate matter using a simultaneous extraction and clean up procedure. The developed SFE method was applied to the analysis of PAH derivatives using GC-ECD and GC-MS. It need not to purify compared with other methods. Yang *et al.* (1995) studied the effect of temperature and modifier on the supercritical CO_2 extraction. They found that properly increasing the temperature and the addition of modifier can increase the recovery of PAHs. The most additive used is methanol. Peltonen and Kuljukka (1995) compared some different pretreatment methods for PAHs and found that SFE has much higher extraction efficiency than Soxhlet extraction.

Wu *et al.* (2006) applied accelerated solvent extraction and analyzed particle size distributions of PAHs in Tianjin, China. Perraudin *et al.* (2005) analyzed particle-bound PAHs using pressurized fluid extraction followed by GC-MS recently. Zhou *et al.* (2005b) also developed a micro pressurized liquid extraction device for the determination of PAHs on PM_{10} samples.

In addition, Koziel *et al.* (2001) improved a needle trap device and commercial poly (dimethylsiloxane) (PDMS) 7- μm film thickness solid-phase microextraction (SPME) fibers for the sampling and analysis of air samples. The air volumes ranged from 0.1 to 50 ml and the sampling times varied from 10 s to 16 min. Results suggested the method should be a simple, fast, reusable and cost-effective screening tool. Kolar *et al.* (2004) also used SPME for atmospheric PAHs and estimated distribution coefficients between air and PDMS coated fiber. But until now, SPME has not been popularly used for the PAHs in the air.

The applications of pretreatment and analytical methods for PAHs in airborne particulates since 2000 are summarized and compared in Table 1. It can be concluded from the table that GC-MS and HPLC are the analytical

Table 1 Applications of pretreatment and analytical methods for PAHs in airborne particulates since 2000

Analyte	Pretreatment method	Analytical method	Reference
13 PAHs	Soxhlet extraction (dichloromethane/acetone = 5 : 1), column chromatography on Al ₂ O ₃ , elute with dichloromethane	GC-MS	Cecinato <i>et al.</i> , 2000
5 PAHs	Soxhlet extraction (dichloromethane/acetone = 3 : 1), column chromatography on Al ₂ O ₃ , elute with dichloromethane	GC-MS	Cecinato <i>et al.</i> , 2003
14 EPA-PAHs	Dialysis in cyclopentane/dichloromethane for 48 h, rotary evaporation, GPC and silica gel column clean-up	GC-MS	Soderstrom and Bergqvist, 2004
15 EPA-PAHs	Dialysis in cyclopentane/dichloromethane for 48 h, rotary evaporation, GPC and silica gel column clean-up	GC-MS	Soderstrom <i>et al.</i> , 2005
22 PAHs	Soxhlet extraction by dichloromethane for 8 h, evaporate concentration	HPLC-UVD HPLC-FLD	Kameda <i>et al.</i> , 2005
15 PAHs	Dialysis in hexane for 48 h, silica gel/alumina column clean-up, elute with dichloromethane/hexane, GPC clean-up	GC-MS	Lohmann <i>et al.</i> , 2001
21 PAHs	Soxhlet extraction (<i>n</i> -hexane/dichloromethane, v : v=1 : 1) for 24 h, concentration, clean-up, reconcentration	GC-MS	Tsai <i>et al.</i> , 2002
12 PAHs	Ultrasonic extraction with dichloromethane/acetonitrile, evaporate concentration	HPLC-FLD	Zhu and Wang, 2003
15 PAHs	Ultrasonic extraction with dichloromethane/hexane, rotary evaporation	RP-HPLC-FLD	Li and Ro, 2000
7 PAHs	Ultrasonic extraction with dichloromethane, column chromatography	GC-MS HPLC-FLD	Schnelle-Kreis <i>et al.</i> , 2001
16 EPA-PAHs	Ultrasonic extraction 3 times with dichloromethane, rotary evaporation, silica-alumina column clean-up, elute with dichloromethane/hexane	GC-MS	Guo <i>et al.</i> , 2003
18 PAHs	Ultrasonic extraction with dichloromethane, centrifugation, evaporation under N ₂	HPLC-FLD	Ohura <i>et al.</i> , 2004
51 PAHs	Soxhlet extraction with acetone for 20 h, rotary evaporation, silica gel column clean-up, elute with <i>n</i> -hexane/methylene chloride	GC-MS	Okuda <i>et al.</i> , 2002
21 PAHs	Soxhlet extraction with dichloromethane/ <i>n</i> -hexane for 24 h, concentration, clean-up, reconcentration	GC-MS	Lin <i>et al.</i> , 2002
24 PAHs	Soxhlet extraction with <i>n</i> -hexane for 24 h, rotary evaporation, silica gel column clean-up, elute with <i>n</i> -hexane/toluene	GC-MS	Tsapakis and Stephanou, 2005a
16 EPA-PAHs	No pretreatment method	Pyrolysis/GC-MS	Ochsenkuhn-Petropoulou <i>et al.</i> , 2003
16 EPA-PAHs	Ultrasonic extraction 3 times with dichloromethane	GC-MS	Bi <i>et al.</i> , 2005
14 PAHs	Soxhlet extraction with dichloromethane/petroleum ether for 24 h, rotary evaporation, alumina silica column clean-up, elute with dichloromethane	GC-MS	Vardar <i>et al.</i> , 2004
21 PAHs	Soxhlet extraction with dichloromethane/methanol (9/1), K-D concentration	GC-MS	Possanzini <i>et al.</i> , 2004
12 PAHs	Soxhlet extraction with methylene chloride for 20 h, fractionation	GC-MS	Vasconcellos <i>et al.</i> , 2003
18 PAHs	Microwave-assisted extraction with dichloromethane, rotary evaporation	GC-MS	Lee <i>et al.</i> , 2001
16 EPA-PAHs	Ultrasonic extraction 3 times with dichloromethane, rotary evaporation, silica alumina column, clean-up, elute with dichloromethane/hexane	GC-MS	Bi <i>et al.</i> , 2003
11 PAHs	Ultrasonic extraction with dichloromethane, rotary evaporation	GC-MS	Chetwittayachan <i>et al.</i> , 2002
15 PAHs	Soxhlet extraction with dichloromethane/petroleum ether for 24 h, K-D concentration, alumina silica column clean-up, elute with dichloromethane	GC-MS	Bae <i>et al.</i> , 2002
16 EPA-PAHs	Extraction with methylene chloride, concentration	HPLC-UVD	Lee and Lee, 2004
8 PAHs	Subcritical water extraction, transfer into dichloromethane, concentration	GC-MS	Romero <i>et al.</i> , 2002
16 EPA-PAHs	Micro pressurized liquid extraction	GC	Zhou <i>et al.</i> , 2005b
16 EPA-PAHs	Ultrasonic extraction with dichloromethane, evaporation	HPLC-FLD	Venkataraman <i>et al.</i> , 2002
16 EPA-PAHs	Ultrasonic extraction 3 times with dichloromethane, rotary evaporation, silica column clean-up	GC-MS	Duan <i>et al.</i> , 2005
16 EPA-PAHs	Accelerated solvent extraction with dichloromethane, clean-up	GC-MS	Wu <i>et al.</i> , 2006
16 EPA-PAHs	Ultrasonic extraction 3 times with dichloromethane, rotary evaporation, silica column clean-up, elute with hexane/dichloromethane	GC-MS GC-FID	Niu <i>et al.</i> , 2005
13 PAHs	Pressurized fluid extraction	GC-MS	Perraudin <i>et al.</i> , 2005
16 EPA-PAHs	Soxhlet extraction with dichloromethane and dimethylsulfoxide for 18 h, concentration, silica gel column clean-up	GC-MS	Dallarosa <i>et al.</i> , 2005
12 PAHs	Ultrasonic extraction with acetonitrile, rotary evaporation	RP-HPLC-FLD	Terzi and Samara, 2005
9 PAHs	Ultrasonic extraction twice with benzene/ethanol (3/1), evaporation	HPLC-FLD	Tang <i>et al.</i> , 2005
16 EPA-PAHs	Ultrasonic extraction 3 times with dichloromethane, K-D concentration	HPLC-FLD	Zhang <i>et al.</i> , 2005
13 PAHs	Supercritical fluid extraction	HPLC	Jonker <i>et al.</i> , 2005
16 EPA-PAHs	Ultrasonic extraction	HPLC-FLD HPLC-UVD	Sanderson and Farant, 2005
15 PAHs	Ultrasonic extraction 3 times with dichloromethane, column separation, rotary evaporation	GC-MS	Tan <i>et al.</i> , 2005
23 PAHs	Soxhlet extraction with dichloromethane/acetone (4/1), evaporation, alumina column chromatography, elute with dichloromethane	GC-MS	Yassaa and Cecinato, 2005
24 PAHs	Soxhlet extraction with <i>n</i> -hexane for 24 h, rotary evaporation, silica gel column clean-up, elute with <i>n</i> -hexane/toluene	GC-MS	Tsapakis and Stephanou, 2005b
17 PAHs	Ultrasonic extraction with dichloromethane, rotary evaporation, silica gel column clean-up, elute with dichloromethane	GC-MS	Zhou <i>et al.</i> , 2005a
16 EPA-PAHs	Soxhlet extraction with dichloromethane/ <i>n</i> -hexane (1/1) for 8 h, rotary evaporation	GC-MS	Bourotte <i>et al.</i> , 2005

Table 1 (continued)

Analyte	Pretreatment method	Analytical method	Reference
36 PAHs	Soxhlet extraction with dichloromethane for 24 h, rotary evaporation, alumina column clean-up, elute with dichloromethane/hexane	GC-MS	Gigliotti <i>et al.</i> , 2005
21 PAHs	Ultrasonic extraction with dichloromethane, centrifugation, evaporation under N ₂	HPLC-FLD	Ohura <i>et al.</i> , 2005
15 PAHs	Ultrasonic extraction 3 times with dichloromethane, rotary evaporation, silica gel column separation	GC-FID GC-MS	Zheng <i>et al.</i> , 2000
10 PAHs	Ultrasonic extraction with dichloromethane, K-D concentration	GC-MS	Li <i>et al.</i> , 2004
11 PAHs	Soxhlet extraction with dichloromethane/cyclohexane for 3 h, evaporation	RP-HPLC-FLD	Besombes <i>et al.</i> , 2001
30 PAHs	Ultrasonic extraction with dichloromethane, rotary evaporation, clean-up	GC-MS	Naumova <i>et al.</i> , 2003
16 EPA-PAHs	Ultrasonic extraction with dichloromethane, evaporation	GC-MS	Park <i>et al.</i> , 2002
14 PAHs	Ultrasonic extraction 3 times with dichloromethane, rotary evaporation	GC-MS	Chen <i>et al.</i> , 2005
16 EPA-PAHs	Soxhlet extraction with dichloromethane, rotary evaporation, clean-up	HPLC-PAD/FLD GC-MS Biological analysis	Ciganek <i>et al.</i> , 2004

methods mostly used; Soxhlet extraction and ultrasonic extraction are the extraction methods mostly applied in the pretreatment.

3 Expectations

Atmospheric PAHs pollution has become a serious problem in the world. More and more researchers have put effort into this field. Though there are many reports on toxicity, concentration, distribution of PAHs and their derivatives, there are still many unknown mutagenic compounds of PAHs which are too low to be detected but have high mutagenicity. How to avoid the volatilization and loss of PAHs in the sampling, the reaction between PAHs and other compounds and the redistribution among different size particles; and how to develop new, noiseless and lower-volume sampler; to realize the pretreatment automatically, innocuously, rapidly, low-cost; to protect people's health from PAHs; all these problems need further endeavors.

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